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(54) A METHOD OF BONDING POLYVINYL CHLORIDE TO A SUBSTRATE

(71) We, HOECHST AKTIENGESELLSCHAFT, formerly Farbwerke Hoechst Aktiengesellschaft, vormals Meister Lucius and Brüning, a German body corporate, of Frankfurt/Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of bonding plasticized polyvinyl chloride (PVC) either to itself or to other materials.

Solvent adhesives are known for bonding all kinds of materials. The basic components of these solvent adhesive compositions are elastomers such as polychloroprene, butadiene-styrene copolymers, butadiene-acrylonitrile rubber (hereinafter referred to as nitrile rubber), polyurethane rubber, butyl rubber or natural rubber. Considerable difficulties are encountered when using polyurethane adhesives and nitrile rubber adhesives owing to their insufficiently long "open time". By "open time" is meant the length of time after application of the adhesive within which two surfaces can be firmly bonded together by light contact pressure. This open time as well as the bond strength both in the cold and heat of all known adhesive systems except those based on nitrile rubber and polyurethane rubber can be varied within wide limits and adapted to the particular purpose by adding suitable natural or synthetic resins. However the addition of such resins which improve the use properties of most contact adhesives, for example polychloroprene based adhesives, has only a slight effect on polyurethane and nitrile rubber adhesives.

Adhesives based on predominantly linear polyurethanes and nitrile rubber have been in use for some considerable time for bonding plasticizer-containing synthetic resins which have difficult adhesion properties, such as soft PVC. In contrast to other contact adhesives, they have excellent resistance to many of the plasticizers conventionally used in synthetic resins and are also resistant to vegetable and mineral oils and fats.

Although the polyurethanes obtained by reacting polyvalent isocyanates with higher molecular weight polyesters containing hydroxyl groups as well as nitrile rubber are compatiblue with the resins conventionally used in the adhesives industry (for example terpene phenol resins, alkyl phenol resins and colophony derivatives), their adhesive contact time is not increased by the addition of such resins. Once the solvent has evaporated, which often takes place very rapidly, and the polyurethane adhesive has therefore dried, no contact adhesive power remains. Thus the operation of bonding together two surfaces which have been coated with a film of adhesive in most cases includes a step of thermal activation, i.e. the action of heat on the solvent-free, dry film of adhesive, which causes the film to remelt and become tacky again so that the surfaces can be bonded together.

Attempts have also been made to improve the adhesive properties of polyurethane and nitrile rubber adhesives by adding polyisocyanates and by applying the adhesives as two-component systems, but these methods also require thermal activation. These adhesives are therefore very restricted in their range of application and cannot be used generally.

We have now developed a resin additive

for solvent adhesives based on polyurethane and nitrile rubber which improves the adhesion and cohesion to PVC containing plasticizers and also increases the adhesive contact time, as defined by the open time, of the adhesive composition.

The invention therefore provides a method of bonding a substrate made of plasticized polyvinyl chloride to itself or to another substrate which comprises applying to the surface of either substrate an adhesive composition comprising a polyurethane elastomer or nitrile rubber elastomer, a resin selected from

a) a novolak derived from an aldehyde and a phenol component as herein defined selected from a bisphenol, an alkylphenol containing at least 3 carbon atoms in the alkyl group, an aralphenol, a mixture thereof and a mixture of at least one of the said phenols with up to 50 mol percent of phenol and/or an alkylphenol containing 1 or 2 carbon atoms in the alkyl group, said novolak being free from hexamethylenetetramine,

b) a halogenated hydrocarbon resin or a copolymer of vinyl chloride and vinyl acetate, and

c) a mixture of the resins a) and b), and a solvent; and bringing together the surfaces to be bonded.

One particularly important advantage of the adhesive compositions used in the method according to the invention is the substantial increase in the adhesive contact time. In addition, the adhesive and cohesive properties of the adhesives are improved. The bonds obtained with these combinations have increased heat resistance, i.e. increased resistance of the bonded joint to the action of heat. When the joints are tested for their shear strength, the material disintegrates. The contact pressure normally required for producing the bond can be reduced when using the method according to the invention.

The linear polyurethanes used for preparing the adhesives are suitably addition products of aromatic diisocyanates and polyesters with terminal hydroxy groups for example the esterification products of dicarboxylic acids with diols. These products are for example polyester which have been cross-linked with isocyanates. The nitrile rubbers used generally have an acrylonitrile content of 25 to 40% by weight, preferably 28 to 39% by weight.

The solvent adhesives employed in the method according to the invention advantageously contain from 2 to 100% by weight, and preferably from 10 to 70% by weight of the resin additives or mixture according to the invention, based on the quantity of polyurethane or nitrile rubber elastomer contained therein.

Suitable aldehydes for preparing the phenol resins used in the adhesives for use according to the invention are, for example, acetaldehyde, butyraldehyde, isobutyraldehyde, chloral and particularly formaldehyde. Suitable phenol components for preparing these phenol resins are for example alkyl phenols, such as *p*-tert-butylphenol, *p*-amylphenol, *p*-isooctylphenol, *o*- and *p*-nonylphenol, dodecylphenol, *p*-cyclohexylphenol, *o*- and *p*-phenylphenol, cumylphenol and phenol components obtained by reacting olefinically unsaturated hydrocarbons such as styrene, α-methylstyrene, the various vinyl toluenes, terpenes, such as turpentine oil, α- and β-pinene or cyclopentadiene and its oligomers, with phenols and particularly with phenol itself. Other suitable phenol components include bisphenols such as diphenylolmethane, diphenylolethane, diphenylolbutane, diphenylolisobutane, and particularly diphenylolpropane; and mixtures of one or more of the above mentioned phenols with phenol, cresols and/or xylenols. Novolaks obtained from phenols and/or bisphenols may also be subsequently substituted by reacting them with the above mentioned hydrocarbons in the presence of proton acids or Lewis acids. In cases where alkylphenols are used, the alkyl group is usually in the *p*-position and preferably contains from 3 to 12 carbon atoms. The term "alkyl" used herein includes cycloalkyl groups. The novolaks are frequently novolaks of formaldehyde and bisphenols, mixed novolaks of formaldehyde with phenols and bisphenols on the one hand and alkylphenols containing at least 3 carbon atoms in the alkyl group or arylphenols or mixtures thereof on the other hand, or substituted novolaks which have been obtained from novolaks of phenol and formaldehyde by subsequently alkylating them in the nucleus with the above mentioned unsaturated hydrocarbons.

Hydrocarbon resins which contain halogen atoms, for example bromine or chlorine atoms, such as chlorinated natural rubber or chlorinated polypropylene as well as polymerisation resins such as copolymers of vinyl chloride with vinyl acetate in a ratio of from 1:0.1 to 1:0.5, preferably from 1:0.15 to 1:0.3 parts by weight, may also be used as additives according to the invention.

The additives used according to the invention are odourless and tasteless and normally do not cause any discolouration of the bonded joint. They may be used either separately or as mixtures with each other in the adhesives used according to the invention. They are compatible with polyurethane and nitrile rubber elastomers and do not reduce the resistance of the adhesives to plasticizers.

Although resol type phenol resins in many cases also increase the adhesive contact time, they have certain disadvantages, for example their odour and their effect on discolouring the film of adhesive.

Preferred solvents for the compositions employed by the method according to the invention are ketones, for example acetone and

methyl ethyl ketone, esters, for example ethyl esters, chlorinated hydrocarbons and aromatic hydrocarbons. They are generally used as mixtures of varying composition depending on the particular technical purpose.

The adhesives, may be applied in the method according to the invention by any of the usual methods, for example by crush coating, application with a coating knife or by spraying, and it is not necessary to modify in any way the subsequent processing of surfaces treated with adhesive. However longer waiting times can be tolerated owing to the increased adhesive contact time.

The process of bonding with these adhesive combinations is therefore much easier because the heat previously required for reactivating the adhesive is no longer necessary. However there is no objection to the additional application of heat.

Moreover the adhesive compositions render the process more economical since there are fewer rejects due to faulty bonding as a result of the longer open time. In addition, the heat resistance can be improved by brief exposure to air at 90° C.

The adhesive mixtures used according to the invention substantially improve the possibilities of bonding plasticized PVC both to itself and to other materials such as polyurethane based artificial leather, rubber, leather, metals, textiles, and cellulosic materials such as wood, paper and cardboard.

The adhesive mixtures according to the invention provide very high resistance to organic solvents, water, oil and fat as well as resistance of the bond to heat. These properties are not deleteriously affected by the addition of polyisocyanates.

The following Examples serve to illustrate the adhesive compositions according to the invention.

The quantities and percentages given below are by weight, and the abbreviation P indicates parts.

Examples.

Preparation of resins:

Resin A

457 P of diphenylolpropane, 150 P of toluene, 180 P of aqueous formaldehyde (30%) and 9 P of oxalic acid are boiled under reflux for 5 hours. 168 P of water and the remaining toluene are then distilled off azeotropically at normal pressure. After the sump temperature has reached 180° C., the solvent residues are removed by distillation under reduced pressure for one hour. 474 P of a pale yellow novolak melting at 116° C. are obtained.

Resin B

456 P of diphenylolpropane, 400 P of a solution of 280 P of 2,6 - dimethylol - 4- nonyl - phenol in 150 P of xylene, 95 P of aqueous formaldehyde (30%), 50 P of xylene and 2.6 P of phosphoric acid are boiled under reflux for about 3 to 5 hours with stirring. The reaction mixture is subjected to azeotropic distillation with continuous return of the non-aqueous phase until no more water separates off. The xylene is then distilled off until the sump temperature reaches 180° C. A water jet vacuum is applied to remove residues of solvent. 720 P of a solid novolak with a melting point of 107° C. are obtained.

Examples 1 to 16 (see Tables).

25 to 50 P of each of the above mentioned products, and 20% solutions of chlorinated rubber with a chlorine content of 62 to 66%, chlorinated polypropylene with a chlorine content of 65 to 68% and a polyvinyl chloride/ polyvinyl acetate copolymer mixed in a ratio of about 1:0.20, in toluene were each separately worked up with a predominantly linear polyurethane consisting of a mixture of a hydroxyl group containing polyester of aliphatic dicarboxylic acids and diols and aromatic diisocyanates to produce adhesives having the compositions indicated in Table 1 (Examples 1 to 10).

500 P of a solvent mixture consisting of 250 P of methyl ethyl ketone, 167 P of ethyl acetate and 83 P of toluene, were mixed with 25 to 50 P of each of the additives indicated above and 100 P of the polyurethane.

The percentages of chlorinated rubber and the like given in the following Tables refer to percentages of the solid substances.

The components were vigorously mixed with stirring and had a solids content of from 20 to 24% by weight, with a viscosity of about 1500 cP at 20° C.

Experiments were carried out to determine the peel strength i.e. the pulling force which must applied normal to the bond to break the bond, of the polyurethane based adhesives of Examples 1 to 10, and also of the adhesives of Examples 4, 8 and 10 reinforced with triphenylmethane - 4,4,4″ - triisocyanate (Examples 11 to 13). In addition, 100 P of a slightly discolouring butadiene-acrylonitrile copolymer (Mooney plasticity ML—4′, 100° C.:65±7) with an acrylonitrile content of about 39% were combined with 45 P of resin B, chlorinated polypropylene and polyvinyl chloride/polyvinyl acetate copolymer and 500 P of a mixture of 3 P of ethyl acetate, 1 P of acetone and 1 P of toluene and the peel strengths were determined (Examples 14 to 16).

Commercial polyvinyl chloride at various concentrations with varying plasticizer contents was used as the test material. Samples were prepared by applying the adhesives over strips 2 × 10 cm in size with a brush. The adhesive contact time was determined by placing the sample strips together after various lengths of time and applying a pressure

of 3 kg/cm² for 10 seconds. After varying ageing times, the bonds were tested for their peel strength and shearing strength at room temperature and at elevated temperatures, using a tension testing machine suitable for the range to be tested and operating at a feed of 180 mm/min.

For comparison, a terpene phenol resin with a melting point of 120 to 130° C. and an acid number of 60 (comparison Example 1) and an alkylphenol resin which was strongly basic in reaction and had a melting point of 65—75° C. (comparison Example 2) were used (see Tables 1 and 2) in the place of the resin additives used according to the invention.

The results are summarised in the Tables. In Tables 2 and 4, the experimental series for 10 minutes exposure to air at 90° C. has been added to demonstrate that the use of additives according to the invention does not afford any disadvantages even when the adhesive is exposed to air at 90° C. and in fact provides some advantages.

TABLE 1

Peel strength (kp/cm)

Air exposure time			20'	1^h	3^h	6^h	1^h
Air exposure temperature			20°C				
Age of bond			7 days				
Test temperature			20°C	20°C	20°C	20°C	50°C
Example		Polyurethane with Novolak*)					
1)	+	25% resin A	5.8	5.9	1.8	—	2.3
2)	+	50% resin A	6.1	5.8	4.9	1.8	3.2
3)	+	25% resin B	6.5	6.5	3.3	—	2.7
4)	+	50% resin B	7.1	7.0	7.0	6.5	3.5
		Polyurethane with halogen-containing polymers of copolymers*)					
5)	+	25% chlorinated rubber	6.5	4.6	—	—	2.5
6)	+	50% chlorinated rubber	7.7	7.8	7.6	—	3.3
7)	+	25% chlorinated polypropylene	6.2	6.1	—	—	2.6
8)	+	50% chlorinated polypropylene	7.8	7.9	5.8	—	3.7
9)	+	25% copolymer of PVC and polyvinyl acetate	6.0	6.1	5.9	—	2.7
10)	+	50% copolymer of PVC and polyvinyl acetate	7.4	7.6	7.5	7.5	3.9
		Comparison Examples relating to 1 to 10					
		Polyurethane without resin or additive	—	—	—	—	—
	+	50% resin comparison Example 1	—	—	—	—	—
	+	50% resin comparison Example 2	—	—	—	—	—

*) For bonding soft PVC containing 40% plasticizer, 2 mm in thickness

— = no bond obtainable, film of adhesive completely dry

TABLE 2

Shear strength (kp/cm²)

Bonding of soft PVC containing 40% plasticizer, 2 mm in thickness

Air exposure time		20'		20'		1h		10'	
Air exposure temperature		20°C		20°C		20°C		90°C	
Age of bond		20'		7 days		3 days		3 days	
Test temperature		20°	50°	20°	50°	20°	50°	20°	50°
Example	Polyurethane								
4)	+ 50% resin B	2.2	0.6	8.8_M	1.1	9.0_M	1.8	9.2_M	1.9
8)	+ 50% chlorinated polypropylene	4.0	0.6	8.7_M	1.3	8.5_M	1.3	9.3_M	2.3
10)	+ 50% copolymer of PVC and polyvinyl acetate	2.4	0.7	8.7_M	1.1	8.3_M	1.1	8.9_M	1.5
	Comparison examples								
	without resin	–	–	–	–	–	–	8.8_M	1.2
	+ 50% resin comparison Example 1					–	–		
	+ 50% resin comparison Example 2					–	–		

M = material disintegrates

– = no bond obtainable, film of adhesive completely dry.

TABLE 3

Peel strength (kp/cm)

After reinforcement with 5%, based on the mixture of solvent adhesive, of a 20% solution of triphenylmethane-4,4',4''-triisocyanate in methylene chloride

Bonding of PVC floor covering containing 10% of plasticizer						
Air exposure time		20'	1^h	3^h	6^h	
Air exposure temperature		20°C				
Age of bond		7 days				
Example	Polyurethane					Pot life
11)	+ 50% resin B	7.1	7.2	7.3	7.0	approx. 3 days
12)	+ 50% chlorinated polypropylene	8.7	8.0	7.0	4.0	approx. 3 days
13)	+ 50% copolymer of PVC + PVAC*	7.0	6.3	6.0	6.2	approx. 3 days
	without resin	3.5	–	–	–	approx. 3 days

– = no bonding possible, film of adhesive completely dry

* = polyvinyl acetate.

TABLE 4

Peel strength (kp/cm)

Bonding of PVC floor covering containing 10% plasticizer						
Air exposure time		10 min	1^h	3^h	10 min	10 min
Air exposure temperature		20°C	20°C	90°C	90°C	90°C
Age of bond		3 days				
Test temperature		20°C	20°C	20°C	20°C	50°C
Example	Butadiene-acrylonitrile copolymer					
14)	+ resin B	2.6	2.8	3.0	2.7	0.4
15)	+ chlorinated polypropylene	1.6	1.8	2.1	2.6	0.6
16)	+ copolymer of PVC with polyvinyl acetate	1.9	1.9	1.9	2.2	0.3
	without resin	–	–	–	0.5	0.1

– = no bonding possible, film of adhesive completely dry

WHAT WE CLAIM IS:—

1. A method of bonding a substrate made of plasticized polyvinyl chloride to itself or to another substrate which comprises applying to the surface of either substrate an adhesive composition comprising a polyurethane elastomer or nitrile rubber elastomer, a resin selected from

a) a novolak derived from an aldehyde and a phenol component as hereinbefore defined selected from a bisphenol, an alkylphenol containing at least 3 carbon atoms in the alkyl group, an arylphenol, a mixture thereof, and a mixture of at least one of the said phenols with up to 50 mol percent of phenol and/or an alkylphenol containing 1 or 2 carbon atoms in the alkyl group, said novolak being free from hexamethylene-tetramine,

b) a halogenated hydrocarbon resin or a copolymer of vinyl chloride and vinyl acetate, and

c) a mixture of the resins a) and b), and a solvent;

and bringing together the surfaces to be bonded.

2. A method as claimed in claim 1 wherein the polyurethane elastomer is based on a polyester with terminal hydroxyl groups and an aromatic diisocyanate.

3. A method as claimed in claim 1 or claim 2 wherein the resin is a chlorinated rubber or chlorinated polypropylene.

4. A method as claimed in claim 1 or claim 2 wherein the resin is a copolymer of vinyl chloride and vinyl acetate in a ratio of from 1:0.1 to 1:0.5 parts by weight.

5. A method as claimed in claim 4 wherein the resin is a copolymer of vinyl chloride and vinyl acetate in a ratio of from 1:0.15 to 1:0.3 parts by weight.

6. A method as claimed in claim 1 or claim 2 wherein the resin is a novolak.

7. A method as claimed in claim 6 wherein the novolak is derived from formaldehyde and a phenol component.

8. A method as claimed in claim 7 wherein the phenol component is a reaction product of a phenol and an olefinically unsaturated hydrocarbon.

9. A method as claimed in claim 7 wherein the phenol component is a phenol substituted in the para-position by an alkyl group containing from 3 to 12 carbon atoms.

10. A method as claimed in any of the preceding claims wherein the resin content is from 2 to 100% by weight based on the weight of the said elastomer.

11. A method as claimed in claim 10 wherein the resin content is from 10 to 70% by weight.

12. A method according to claim 1 substantially as herein described.

13. A method of bonding a substrate made of plasticized polyvinyl chloride to itself or to another substrate substantially as herein described in Examples 1 to 16.

14. Substrates bonded together by a method as claimed in any of the preceding claims.

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